MERCURY
THE TWILIGHT

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MERCURY: THE TWILIGHT

A Review of the Laboratory Services Branch Mercury Laboratory work since 1974.

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MERCURY - THE TWILIGHT

Since we last got together in 1974 the whole field of mercury pollution has undergone a great change. Gone are the daily crises, the strident voices from the field all claiming to have found the next Minamata, and the activist groups accusing us of cover-ups, shake-downs and side-steps.

The crises never existed, as it turns out. No equivalent of Minamata occurred on this side of the ocean. The activist groups have melted away and environmental matters seldom occupy the front pages in these times of inflation and cutbacks. This is not to say that the mercury problem never existed, or that it is cleaned up. However, in many instances the degree of mercury contamination is less than it was just 5 years ago, and in some instances it is remarkably lower today.

This report will deal with several aspects of the MOE's mecury involvement over the past years, and will attempt an update of significant changes in attitudes, policies, and levels concerning mercury.

1 - Chlor-alkali Plants

Perhaps the most significant single thing that occurred in the mercury field over the past 5 years was the decline in the industrial use of mercury. In 1970 there were 6 chlor-alkali mercury cell plants in Ontario. These were located at Thunder Bay, Marathon, Dryden, Sarnia, Hamilton, and Cornwall. Today there is 1, at Cornwall. The usage of mercury in this field has dropped accordingly, and similar reductions have occurred in slimicide and preservative usage. Generally, the overall use of Hg in industry is lower by a large but known factor since 1970. This is reflected in the steadily declining price of the metal on world markets; in 1968 a flask (76 lbs) was $550, today the price is around $120 per flask. Its use in many fields, from electrical and industrial control is continuing to decline as substitutions eliminate the liquid element.

The irony is that as the price of Hg drops, its attractiveness as an industrial agent will strengthen.

2 - Legal Actions

During the past year there has been considerable activity regarding litigation in the field of mercury pollution. However, none of these resulted in decisions against alleged polluters, except for a relatively minor case at Marathon involving American Can Corporation. A most significant decision regarding litigation was the Dow Court Case decision. In a statement by the

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Honourable Roy McMurtry in June, 1978, the Government of Ontario dropped its case against the Dow Chemical Company of Canada. It was the opinion of J.J. Robinette, who handled the litigation for the Government that the case could not be continued further. All claims of the fishermen had been settled by Dow, and Dow had spent an estimated $40,000,000 in converting to processes which do not use mercury. Regarding negligence on Dow's part, Mr. Robinette felt that there was no evidence of negligence on Dow's part in controlling waste following revelation of the mercury problem in 1979. The question of whether or not Dow should have appreciated prior to 1969 the potential hazards of discharging mercury cannot be adequately answered, since there is no way of establishing whether or not Dow were aware of European studies prior to 1969. Regarding the claim of nuisance, Mr. Robinette advised that the Government had a reasonably arguable case but by no means a clear one. His unequivocal recommendation was to discontinue the action against Dow, and this was done in June, 1968.

The only other court case involving mercury is that of AMOG (Anti-Mercury Ojibway Group), a group of Indians, lawyers, and others who were attempting to amass data to launch lititgation against Reed Pulp and Paper in Dryden. This effort appears to have fizzled out, since there is inadequate funding and MOE are unaware of any further developments in this case.

3 - Changes in Guidelines

A - In the past 5 years there have been several new approaches taken in the setting of fish consumption guidelines. Up to this time it has been the general case for most countries to apply a limit of 0.5 mg/kg mercury as the limit for fish sales or fish consumption. This number had been developed using the traditional method based on maximal allowable concentrations (MAC). However, the number arrived at of 0.5 mg/kg proved unreasonable when one considered the number of lakes where fish commonly had levels in excess of the guidelines and when one considered fish consumption patterns among Ontario residents and anglers.

Methylmercury is bioaccumulative, that is, it tends to increase up the freshwater trophic scale, so that large, predatory fish have higher mercury concentrations than small or non-predatory fish. Usually, a reasonably well defined relationship exists between mercury level and fish size, characteristic of both the species and water body. Under the conventional approach, if fish were sampled from a watercourse, the average mercury concentration could easily exceed the 0.5 mg/kg guideline if the sample consisted of large predators, even though smaller fish or non-predatory species were well within the guideline. The new guidelines, therefore, were to be location, species, and size specific.

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Another factor to be considered was the eating pattern associated with freshwater fish. The majority of people consuming these fish would do so during the course of a two or three week fishing trip. Few Ontario residents rely on freshwater fish as a staple of diet. Medical studies on people in methylmercury poisoning episodes in Japan and Iraq had determined that a body burden in excess of 20 mg of methlymercury was required prior to the onset of symptoms. Further studies using radiolabelled methylmercury on human volunteers had established that methylmercury has a half-life in the body of some 70 days. Using this information, it became obvious that short term consumption of mercury contaminated fish with concentrations well in excess of 0.5 mg/kg could be tolerated without the body burden reaching even 5 mg, well below the lowest level associated with any toxic symptoms.

The new guidelines (outlined in detail in "Health Implications of Contaminants in Fish") incorporate all of these data. To determine allowable consumption of frewshwater fish, the consumer would consult the species chart for the relevant water body, which classified different species by size range and mercury level. Then, the consumer would consult the regulations under the length of time he will be consuming the fish, and is advised of the number of meals per week he may safely eat.

These new guidelines embody the rational use of available information on mercury levels in fish, and duration of consumption, enabling the safe utilization of Ontario's most delicious natural resource.

B - A major change in consumption guidelines also occurred in the U.S. In the U.S., the guideline of 0.5 mg/kg was changed to 1.0 mg/kg. This was forced by the U.S. district court in Florida following a court decision between the U.S. Government (Health and Welfare) and Andersen Seafoods Incorporated (Plaintiffs). The decision concerned the following items:

i the meaning of the word "adultered". Basically the argument concerned the impossibility of determining what portion of mercury in swordfish is due to anthropogenic activities.

ii Analytical error - it was found that the FDA Laboratories had an error ranging from 0.5 to 1.1 ppm on the same sample of swordfish.

iii The amount of methylmercury in fish.

iv The acceptable weekly intake (AWI). This was determined to be 840 mm per week as methylmercury which in turn was raised to 933 mm to convert to total mercury, assuming that 90% of the mercury in fish flesh is present as methylmercury.

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v - The MECCA fish consumption study. MECCA is the acronyn for Model for Estimation for Consumption of Contaminants from Aquatic Foods. Based on established fish consumption patterns in the U.S. it was established that as much as 1.99 mg per week could be consumed if the level was 1.0 ppm per week AWI. However, the plaintiff argued if all swordfish with more than 1.0 ppm were removed from the market, the average mercury in swordfish would be approximately 0.80 ppm.

The final decision was as follows: swordfish containing 1.0 ppm or less of mercury cannot be deemed to be adultered. All court costs were taxed against the defendant (USHEW). Based on this the U.S. Federal Register on January 19th, 1979, changed their regulation to 1.0 mg/kg mercury in fish. It is worth noting that while selenium was mentioned in the Federal Register, it did not play any role in the change in the guidelines. The following quotation is from the Federal Register for the day:"although much work has been done in the area of mercury/ selenium relationships and there appears to be some mechanism in fish for protection against methyl-mercury toxicity in animals, whether or not selenium is protective is not clear. The participants in the workshop concluded that the findings to date are inconclusive".

4 - Declining Mercury in Fish

The basis for a reduction of the mercury content in fish only became apparent in 1974. Prior to this, it had been thought that waterways contaminated by mercury would remain so for 50 to 500 years, depending upon the expert. Some work in Sweden suggested fish downstream from mercury-slimicide users could recover (decline in mercury content) but data were scarce. Since then, MOE staff have closely monitored fish mercury levels in several major Ontario water-bodies, in an attempt to determine whether declines in mercury contamination were occurring, and if so, at what rate.

A - Lake St. Clair

The best example of a mercury-recoverd water-body is Lake St. Clair, located between Lakes Huron and Erie. Between 1948 and 1970, thousands of pounds of mercury were discharged to the St. Clair River. The major contributor to the mercury pollution of the St. Clair River and Lake St. Clair was identified as the Dow Chemical Chlor-Alkali complex at Sarnia. It is estimated that the losses of mercury averaged 35 pounds per day in 1969.

In March, 1970, the Ontario Water Resources Commission (now part of the Ministry of the Environment) issued an order requesting the cessation of mercury discharge, and losses of mercury were curtailed. Since May of 1970, mercury discharges to the St. Clair River have been negligible.

Since 1970, over 12,000 fish representing 31 species have been collected and analyzed. These can be compared by looking at average levels, or by statistical treatment. The mercury concentration in fish muscle is usually correlated to the size of the fish. Comparing fish from year to year or lake to lake requires the elimination of variation due to differences in mean fish size. This is most readily done by selecting a standard size for the species of interest, and comparing the mercury concentration of that size from year to year. The mercury concentration of the standard sized fish is determined from the log-log transformed regression of mercury concentration on fish length.

Examination of the data collected reveals several interesting findings. For several of the key species from Lake St. Clair, there was sufficient data from 1970 to 1976 to allow a comparison in the mercury concentrations over the years. As noted previously, the mercury concentration is correlated to fish size. Valid comparisons from year to year, therefore, should be done only between fish of equal length or weight. To do this, regressions were done for each of the species for each year for which sufficient data base was available. The estimate of the mercury concentration at a particular length or weight from the geometric regression, for each year was then plotted. The plots of the estimated mercury concentrations for a specified length or weight of several species of fish indicate definite tendencies towards lower mercury levels. For example, a 40 cm walleye in 1970 had a mean mercury level of 2.1 ppm; in 1976 the level for the same sized walleye had fallen to 0.56 ppm. Similar observations can be made for all of the species examined at various sizes.

Another way of examining the loss of mercury is to compare the mean mercury level for a given year class of fish for a specified year, to the mercury level for the next subsequent year class in the next subsequent year. For example the estimated mercury level in one-year old walleye in 1970 was 1.6 ppm. In 1971, these walleyes would be two years old. Two year old walleye in 1971 had 1.55 ppm mercury. In 1972, three-year old walleye had an estimated 1.37 ppm mercury.

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The mean lengths for each class of walleye were derived from the 1973 collection for which age data was available. By plotting age against length for the large 1973 sample, an estimate was made of the approximate length for a given year class. The length data, now associated with a specific year class, was used to calculate the mean mercury concentration from the existing regressing lines between fish length and mercury concentration, thereby providing an approximation of the mercury concentration associated with a given year class of fish, for any specified year. The curves show the decreasing mercury levels for the 1970 year class in subsequent years. Besides indicating the dramatic decline in mercury concentrations for similar sizes of fish, the curves can be extrapolated beyond 1976, to predict when the geometric mean of the mercury concentration of a particular length or weight for each species will fall below the 0.5 ppm federal guideline.

It is interesting to note that, using these extrapolations, one could predict the mercury concentration in fish being sampled last year and the year before(1977, 1978). In fact, the values predicted were within an average of 0.01 ppms of the ACTUAL values both years, for all species plotted. This is one of the rare occasions where nature mimicked science. Similar data exists for about 16 other species in this system.

Reasons for the decline in this system include:

1 - Discharge from the Dow chlor-alkali plant in Sarnia was stopped.

2 - When the plant used mercury much of the mercury was probably discharged as soluble forms (most likely as mercury-chloride complexes,Hg-Na-Amalgams and Amalgam - complexes). It has been shown that ionic mercury compounds are much more easily methylated by microorganisms than nonionic forms. It is reasonable to assume, therefore, that sometime between 1970 and 1971 there was a drastic reduction of the amount of readily biotransformable forms of mercury. Since that time, the rate of methylmercury biosynthesis has been so reduced that the rate of mercury accumulation by fish is exceeded by the growth rate of the fish. The net result is that the mercury level in fish has declined over the last nine years.

3 - The mercury that was discharged in insoluble forms has been incorporated into the bottome sediments of the system. In the shallow water environment that characterizes Lake St. Clair and the western basin of Lake Erie, sediments are readily translocated by wave generated currents. Thomas compared 1979 and 1974 mercury concentrations in the

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sediments of of Lake St. Clair and concluded that 64% of the 1970 quantity has been transported downstream to Lake Erie by 1974. It is likely that a considerable portion of the mercury still in Lake St. Clair in 1974 would have been washed out or covered up by 1979.

B - Wabigoon - English River System

This system has been examined since 1969, by many research groups. Some of the best and earliest work was done by FRB Winnipeg and, since 1974, by MOE,Thunder Bay. The regional office has planned surveys, taken samples, and examined all aspects of the mercury problem, including fish, sediments, vegetation and air, and they have been instrumental in mounting one of the most comprehensive environmental surveys in Ontario.

In 1975, B.P. Neary and myself prepared a report that attempted to pull together all existing mercury data on this system. We did this in order to consolidate the large data base that existed, primarily consisting of information from the Federal, Provincial, and University studies that had been on-going since 1969.

Another reason for the report was to attempt to identify the actual source of mercury in the system. Atmospheric sources, mining, slimicide use, and mineralization sources had all been suggested as possibilities.

The major source of mercury contamination in the Wabigoon River, and the English River downstream of Ball Lake, was the Dryden Chemicals chlor-alkali plant in Dryden. The plant had curtailed its mercury release in 1970, and switched to a process not using mercury in late 1975. The only other industrial source of mercury in the area is the Ontario-Minnesota Pulp and Paper Company in Kenora, on the Winnipeg River. It is estimated that this Company used about 18,000 lbs of a slimicide (containing 11,000 lbs of mercury) between 1969 and 1967. Currently there is no known industrial input to these rivers, and the mercury concentrations probably reflect input prior to 1970.

Following 1975, sampling programs for fish surveys were planned by MNR, Regional MOE, and Laboratory Staff for 1976, 1977, and 1978. Regional Thunder Bay Staff have since 1974, planned, collected, and since 1976, analyzed their own water survey samples and major sediment surveys,

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and air surveys have been undertaken by Regional Staff. Reports on the air and sediment surveys have been published annually and are available from the Regional Office.

COMPARISON OF MERCURY CONCENTRATION SINCE 1975.

We have plotted the mercury concentration in standard walleye and pike for each of the lakes for which there was more than two years of data. In the St. Clair system, the cessation of mercury resulted in an immediate exponential decline in the mercury concentration of all species of fish. This is apparently not the case in the Wabigoon-English system.

i - It is tempting to speculate on the lack of definite decline in the mercury levels in fish from the Wabigoon-English. The most obvious difference between the St. Clair and the Wabigoon systems is water flow. There is evidence that much of the mercury contaminated sediment in Lake St. Clair has been transported to the western basin of Lake Erie. At this point, the mercury is fairly widely dispersed, and methylation of the mercury would probably result in only a small elevation in the levels of methylmercury in the large fish population in Lake Erie, and only in areas where natural sinks existed for the mercury contaminated sediment to collect. In fact, data from last year indicate a decline in fish from western Lake Erie despite the fact there is no basin there.

In the Wabigoon system, there is no large basin for the dispersal of mercury. Rather, there is a series of relatively small lakes, each of which will act as a sink or as a barrier in the scouring of mercury laden sediment from the river and Clay Lake. The low flow in the system also slows the scouring process, and probably is reflected in a slower sedimentation rate, which delays the covering of the mercury contaminated sediment with uncontaminated ones.

ii Another explanation for the lack of a decline of mercury concentration in Wabigoon-English system fish may lie in the nature of the particulate matter in this system. In both the Wabigoon-English and St. Clair Rivers, a significant portion of the mercury was lost in the form of highly soluble salts and/or complexes. These forms would tend to be more easily methylated than the less soluble metallic mercury or mercury sulfide forms. Once the ongoing mercury discharges were curtailed one would expect to note a decline in the mercury being accumulated by fish. This is exactly what was recorded in the case of St. Clair fish.

However, in the Wabigoon-English system, the amount of pulp and paper wastes and other particulate metter in the water has been so high that virtually all of the mercury discharged would tend to be immediately bound to or associated with this particulate matter.

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iii - In addition, the coninuous input of pulp and paper wastes and wood fibers from the Reed mill at Dryden provides a favourable medium for the methylation of mercury. This would tend to cause the methylation of mercury. This would tend to cause the methylation rate to remain high regardless of the form in which the mercury was originally discharged, for two reasons. First, the available mercury is associated with finely divided, organic-rich particulate matter. Second, the organic nature of the particulates appears to stimulate methylation. These factors would tend to off-set the effect of cutting off the soluble mercury discharge and would thereby delay the recovery process for the fish in the system.

IN SUMMARY

The levels of mercury in fish from contaminated lakes on the Wabigoon and English River systems have not changed significantly in the past five years. There is evidence of a minor decline from 1976 to 1977 but the rate of change is musch lower than that observed in fish from Lake St. Clair.

It is evident that the cessation of mercury discharges from the chlor-alkali plant in Dryden has not resulted in a rapid decrease in mercury levels in fish. This is probably due to three primary factors: the relatively low water flows in the system, which results in a slow dispersal of the mercury; the low rate of covering of the contaminated sediments; and the heavy loading of organic particles to the system by Reed's plant in Dryden.

Yearly surveys of mercury levels in fish from the affected lakes are felt to be unnecessary. The data so far indicates that the decline in mercury concentrations in fish will be much slower than the decline in St. Clair fish, so that surveys every two or three years should suffice for the purpose of monitoring the trend.

C - Lake Simcoe

As far as mercury pollution goes, Lake Simcoe was a non-problem. It only became a "problem" when extremely large walleyes (up to 12 lbs.) were sampled a few years ago and were found to contain over 1 ppm. Such a finding is not suprising considering the size and trophic level of these fish. Similarly large bass, ling, and lake trout were also higher than .5 ppm.

Following examinations of museum fish, water, sewer sludge, golf course samples, goose excrement, and so on the conclusion was made that there was not a mercury problem in Lake Simcoe.

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D - Muskoka Lakes

High levels of mercury were found in trout, small mouth bass and other species in several lakes throughout the Muskokas. The lakes most seriously effected were Mary, Fairy and Lake Vernon. Suggested sources for the elevated mercury in the Muskoka Lakes include

- acid rain
- spot sources or once only mercury emissions
- abandoned mines or industrial sites
- as yet undiscovered natural or anthroprogenic sources.

This problem remains, it shows no signs of diminishing, and deserves further study. In this regard it is similar to the Wabigoon-English situation except that the class of people affected by the mercury fish levels is considerably different.

5 - NEW DEVELOPMENTS IN LSB: MERCURY ANALYSIS AND DATA HANDLING

1) A brief review of the analytical procedure is presented.

2) Automation of the mercury analysis is discussed. Basically automation of mercury analysis was a combination of existing technologies which resulted in the mercury laboratory developing the capacity to analyse 500 mercuries per week with reduced manpower.

3) ALDAS: automated laboratory data acquisitions system. This system has dramatically reduced the amount of technician time required to produce mercury data. The technician now weighs the sample, punches the weight into ALDAS along with the sample number in batches. He digests the samples, loads the tray, and ALDAS does the rest. It checks blanks, standards, SRMs, slopes and makes appropriate corrections. It sequences samples, reads peaks, calculates results and prints out final reports. It transfers data to archives.

The major areas of improvement with ALDAS has been time savings, accuracy and organization. Time savings can be demonstrated in the reduction of technician on-line time in the mercury laboratory being reduced from 5 to 3 technicians.

Accuracy has been improved by the elimination of the manual transfer of data. It was found that most of the errors inherent in the manual system were associated with the reading of peak heights. Anyone who has attempted the rather blinding task of accurately measuring a sequence of 100 peaks has some appreciation of the problems involved. During a period of four weeks when both ALDAS and the manual system were running in parallel, every discrepancy other than those associated with using different calibration procedures was resolved in favour of ALDAS. This increased accuracy is derived from the fact that ALDAS receives data directly from the instrument (FAAS, LDC, or balance) producing the reading, rather than relying on several data transfers; one from the instrument to bench sheet, another from bench sheet to calculator, a third from calculator to result sheet, and a fourth from result sheet to 9830 data base.

The three major areas of improvement have been in time savings, accuracy and organization. Since the system is oriented towards processing batches of samples (1 batch = 1 test tube rack) from a particular location, a new system for keeping track of samples had to be instituted. The new system of record keeping makes it easy to keep track of sample throughput, and results, strip charts, and bench sheets can be retrieved readily from either the "hard" backup on file, or from the archive disks which contain all the information on samples in a machine readable form.

The first stage of expansion of ALDAS to include selenium, arsenic, and antimony has gone very smoothly, so manpower savings in other areas will soon be felt. If expanded disk and keyboard facilities can be purchased, even further savings can be anticipated.

6 - Distribution of Mercury in Fish

Samples of several species of fish were dissected and the muscle, bones and various organs were analyzed for total mercury. Methylmercury was determined on some of the samples as well. Samples were analyzed for total mercury by Hot Block digestion, followed by flameless atomic absorption spectrophotometry. Methylmercury was determined using a modified version of Westöö's technique.

Lipid and water contents of muscle portions were determined by azeotropic distillation with benzene. Lipids and water removed by azeotropic distillation were analyzed for total mercury to establish the absolute amount of mercury in each fraction of the sample. Residual fish muscle retained 99.3%, the lipids held 0.6% and the water only 0.1% of the total mercury in the sample.

Both total and methylmercury were determined on 50 muscle samples for catfish, northern pike, and lake trout. Average methylmercury/total mercury ratios were 91, 90, and 95% respectively.

Fish were longitudinally sectioned, to obtain sample representing various segments of the fish from front to back (anterior to posterior). They were also laterally sectioned to provide samples from internal and external muscle. They were also dissected and heart, kidney, brains, intestines, intestine contents, gonads, skin, eyes, lenses, scales, bones and gills were subsampled.

The mercury concentrations in muscle samples from the tails of the fish were invariably lower than those from the anterior muscle samples. Mercury concentration is generally higher in interior muscle sections for bottom-feeding onmivorous species. For these sample species (channel catfish and carp), there was a negative relationship between lipid content and mercury concentration and a positive relationship between mercury and water concentration in the muscle. Pike, pickerel, and lake-trout (predaceous fish) showed no such significant relationships.

The distribution of mercury in various organs of the fish was as follows for most species, kidney > liver > heart > brain > gonads > intestines. Skin,scales, eyes, bone, and other external parts invariably had less mercury content than muscle from the same fish. Nearly all the mercury in fish muscle was found to be associated with muscle protein rather than lipids or water fractions and was virtually all in the methyl form.

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7 - Mercury/Selenium Relationship

In order to investigate this possibility, two sampling surveys were csrried out. In one, various species of freshwater fish (N. pike, smallmouth bass, carp, etc) with different feeding habits and trophic levels were collected from the Toronto Harbourfront area and from Lake Superior and were analysed for selenium and mercury. These areas were chosen to represent industrialized and non-industrialized situations. The mercury level varied from species to species and between locations for a given species, but the selenium content remained relatively constant. No correlation was found between the selenium and mercury concentrations for any species from either location.

In the second phase of the experiment, one species (Pickerel, Stizostedion vitreum) was collected from several areas of Ontario. The sampling locations were selected to represent industrialized and non-industrialized situations in the Great Lakes and industrialized and non-industrialized locations in non-Great Lakes inland waters. Again, no relationship between selenium and mercury levels in the pickerel was found.

Selenium was found in all fish which were analysed, but in no case did levels approach those which have been reported in marine fish. However, the mercury levels ranged from natural levels to very high (> 5 ppm) concentrations, depending on the location and its degree of industrialization. The variance of these results with respect to those of marine fish researchers may be due to such factors as biological differences, salinity, or availability of these elements in the respective environments.

8 - Mercury in Brain Tissue

This survey involved the sampling of brain, liver, and kidney samples from deceased Canadian Indian residents of Northern Ontario communities, and the sampling of similar material from a control group selected by the Ministry of Labour staff. Significant differences in mercury levels could not be established between the two data sets.

For the samples from the study group, the concentration of total mercury decreased in 16 cases in the order kidney > liver > brain. This corresponds to reports in the literature for both unexposed and exposed individuals.

Body burden of methylmercury was calculated from hair and brain concentrations using relationships reported in the scientific literature. The highest body burden estimated was 5 mg- need 20-40 mg to have symptons.

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A linear relationship was found between the concentrations of total mercury in brain and kidney cortex (Brain: Kidney = 4%, Range 2-92% when all individuals were considered, while no such relationship was found for organic mercury in these tissues.

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